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C. R. Chimie xxx (2017) 1-5



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# Direct carboxylation of aromatic compounds using the sodium hydrogen carbonate/triphenylphosphine ditriflate system

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#### ARTICLE INFO

Article history: Received 11 August 2017 Accepted 30 October 2017 Available online xxxx

Keywords: Triphenylphosphine ditriflate Carboxylic acids Arenes Sodium hydrogen carbonate Electrophilic substitution

#### ABSTRACT

A new procedure was developed for the highly regioselective synthesis of aromatic carboxylic acids using the sodium hydrogen carbonate/triphenylphosphine ditriflate system in ethanol at room temperature. This metal-free system was used for the carboxylation of thiophenol with unexpected products in terms of selectivity. The simplicity of the procedure, readily available aromatic compounds, short reaction times, and mild reaction conditions are other advantages of this protocol.

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#### 1. Introduction

Breaking and functionalization of a C–H bond leading to a new C–C bond formation is a challenging area in organic chemistry [1]. Traditionally, the carbon-carbon bond formation in preparation of aromatic carboxylic acids involves treatment of strongly organometallic compounds such as aryl palladium or aryl magnesium reagent [2] with CO [3] or CO<sub>2</sub> [4]. The use of other substrates such as aryl halides has been reported in carboxylation reactions [5]. Arenes have also been used to produce aromatic carboxylic acids via direct carboxylation of the C-H bond. Carboxylation of arenes with formic acid was developed [6]. It was reported that N-heterocyclic carbene metal complexes can efficiently catalyze carboxylation of heteroaromatic compounds [7]. Carboxylation of benzoxazole and benzothiazole derivatives with CO<sub>2</sub> by heterocyclic copper complexes was reported [8]. Consequently, the introduction of a simple and efficient method without using transition metal and gaseous carbon dioxide or carbon monoxide is desirable, especially using reagents, which are more favorable to handle.

Trifluoromethanesulfonic anhydride,  $Tf_2O$ , is a good reagent for the conversion of an OH group into an OTf leaving group [9]. Triphenylphosphine ditriflate (TPPD) was prepared exothermically as a white precipitate from the reaction of  $Tf_2O$  with Ph<sub>3</sub>PO in CH<sub>2</sub>Cl<sub>2</sub> [10]. This salt was presented as a powerful dehydrating agent and promoter (Scheme 1) [11].

As part of our ongoing efforts to develop electrophilic aromatic substitution [12], we have examined direct carboxylation of arenes using sodium hydrogen carbonate as a carboxylating agent, TPPD as a promoter, and ethanol as a solvent at room temperature under transition metalfree conditions (Scheme 2).

#### 2. Experimental section

#### 2.1. General information

All the chemicals were obtained from Merck, and used as received. All products are known and characterized by a

#### https://doi.org/10.1016/j.crci.2017.10.008

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Please cite this article in press as: M.M. Khodaei, et al., Direct carboxylation of aromatic compounds using the sodium hydrogen carbonate/triphenylphosphine ditriflate system, Comptes Rendus Chimie (2017), https://doi.org/10.1016/j.crci.2017.10.008

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R = H, Br, OH, NO<sub>2</sub>, SH, CI, OMe, F, Me.

Scheme 2. Synthesis of carboxylic acids.

comparison of their spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR) with those reported in the literature. All yields refer to the isolated products. NMR spectra were recorded on a Bruker Avance spectrophotometer (400 MHz) in CDCl<sub>3</sub> and used as an internal standard.

#### 2.2. General procedure for the carboxylation of arenes

The fresh obtained TPPD (0.672 g, 1.2 mmol) was dissolved in 3 mL of ethanol, and then sodium hydrogen carbonate (0.084 g, 1 mmol) was added into the solution. The resulting mixture was stirred for 30 min at room temperature. Then, mesitylene (0.14 mL, 1 mmol) was added into the solution and the stirring continued for 60 min at room temperature. The reaction completion was monitored by thin layer chromatography. After the completion of reaction, the solvent was removed under reduced pressure, and the saturated sodium bicarbonate solution (10 mL) was added to the medium. The product was extracted with chloroform  $(3 \times 5 \text{ mL})$  and the organic layer washed with water and dried over anhydrous MgSO<sub>4</sub>. The filtrate was evaporated and the crude product was purified by silica gel column chromatography using ethyl acetate/n-hexane (3:7) as eluent to afford 2,4,6-trimethylbenzoic acid (0.131 g, 89%).

#### 3. Results and discussion

The initial study was directed toward exploring the reaction conditions for the carboxylation of mesitylene using NaHCO<sub>3</sub>/TPPD system. We first tested the suitability of several different solvents for the carboxylation of mesitylene with NaHCO<sub>3</sub> promoted by TPPD. It was observed that the nature of the solvent has a considerable effect on the reaction rate and the yield of product, and EtOH was found to be the most effective solvent (Table 1, entry 4). Other solvents including H<sub>2</sub>O-EtOH (1:1), H<sub>2</sub>O-EtOH (1:2), H<sub>2</sub>O-EtOH (2:1), CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and CHCl<sub>3</sub> were substantially less effective. Water was not effective at all due to the low solubility of arenes at the reaction temperature. To study the effect of the amount of TPPD, different amounts of the promoter (0.5, 1.0, 1.2, 1.4, and 2.0 mmol) were chosen. The results show that 1.2 mmol of the promoter per millimoles of mesitylene afforded the best results. An increase in the amount of TPPD to 2 mmol shows no significant difference with respect to the yield. The reaction was not complete when less than 1.2 mmol of the promoter was used. An increase in the temperature from room temperature to reflux condition indicates that the yield was almost unaffected. As a result, the optimized reaction conditions are TPPD (1.2 equiv) in EtOH at room temperature. The presence of the promoter is essential to the reaction, because no reaction occurs in the absence of it.

To examine the generality of this procedure, we investigated the reactions using a wide range of arenes as substrates under the present reaction conditions. The results are summarized in Table 2. The carboxylation reaction can be carried out with aromatic compounds without consideration of the type of substituent. Aromatic compounds with both electron releasing and electron withdrawing groups afforded the corresponding products in moderate to

| Table  | 1      |           |       |               |          |                         |
|--------|--------|-----------|-------|---------------|----------|-------------------------|
| Effect | of the | solvent o | ı the | carboxylation | reaction | of arenes. <sup>a</sup> |

| Entry | Solvent                         | Time (min) | Yield (%) <sup>b</sup> |
|-------|---------------------------------|------------|------------------------|
| 1     | H <sub>2</sub> O-ethanol (1:1)  | 120        | 37                     |
| 2     | H <sub>2</sub> O-ethanol (1:2)  | 95         | 67                     |
| 3     | H <sub>2</sub> O-ethanol (2:1)  | 120        | 30                     |
| 4     | Ethanol                         | 60         | 89                     |
| 5     | H <sub>2</sub> O                | 120        | 0                      |
| 6     | CH <sub>2</sub> Cl <sub>2</sub> | 120        | 0                      |
| 7     | MeCN                            | 120        | 0                      |
| 8     | CHCl <sub>3</sub>               | 120        | 0                      |
| 9     | <i>n</i> -hexane                | 120        | 0                      |

<sup>a</sup> Mesitylene (1 mmol), sodium hydrogen carbonate (1 mmol), and TPPD (1.2 mmol) in EtOH at room temperature.

<sup>b</sup> Isolated yield.

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